1768

SOME OBSERVATIONS ON THE FACTORS AFFECTING THE STABILITY OF CHROME LEATHER*

J. H. BOWES

British Leather Manufacturers' Research Association
Milton Park
Egham, Surrey
England

ABSTRACT

The relationship between chrome content and shrinkage temperature has been examined. Under standard conditions of tanning the graph relating shrinkage temperature and the logarithm of the chrome content is a straight line. Neutralization and drying at elevated temperatures decreases shrinkage temperature in relation to chrome content, while the introduction of carboxyl groups by pretannage with formaldehyde plus glycine increases it.

After treatment in sodium lactate solutions there is still a linear relationship between shrinkage temperature and the logarithm of the chrome content, though the line is displaced to lower values of shrinkage temperature.

Drying at high temperatures or incubating at 40°C. slightly increases the resistance of chrome leather to the detanning action of sodium lactate solutions (synthetic perspiration).

The results indicate that the formation of cross links is an important factor governing hydrothermal stability but that unipointly fixed chrome also plays a part. Conditions of processing for optimum hydrothermal stability and resistance to the detanning action of sodium lactate are indicated.

INTRODUCTION

Shrinkage temperature has long been taken as one of the criteria of tannage. It is a somewhat empirical measurement, since the values obtained depend on a number of factors such as pH, rate of heating, and more particularly, the solvent; nevertheless, it is a useful guide to the stability of a leather.

*The work reported in this paper forms part of a research program sponsored by the U. S. Department of Agriculture under the authority of U. S. Public Law 480.

Chrome leather is characterized by a high shrinkage temperature and by its resistance to boiling water. Bowes, Davies, Pressley, and Robinson (1) found that under similar conditions of tanning with chromium sulfate liquors there was a linear relationship between shrinkage temperature and the logarithm of the chrome content, regardless of the final pH of tannage.

In view of the possible variations in size of the chrome complexes and the number of different ways in which the chrome may be present in the leather, e.g., bound to one carboxyl group (unipoint fixation) or to two or more carboxyl groups (multipoint fixation) either in the same or an adjacent polypeptide chain, or merely deposited as a basic salt, it is perhaps surprising that this simple relationship should hold. In particular, one would expect that multipoint-fixed chrome would be the governing factor and that this would be affected by variations in pH. It has been shown, however, that the shrinkage temperature of collagen and leather in a nonaqueous medium increases with decrease in water content (2,3), and Witnauer and Fee (3) have suggested that the decreased accessibility of the fibers caused by tanning contributes to hydrothermal stability. It seems likely that this factor is of importance with chrome leather, especially since evidence suggests that the number of interchain cross links between carboxyl groups is relatively small (see Gustavson [4] for discussion on this point).

Even allowing for both factors being operative, it still seems surprising that the shrinkage temperature is so closely related to the chrome content even under the restricted conditions used by Bowes *et al.* (1). This relationship does not hold for finished leathers from a variety of sources, quite wide variations in shrinkage temperature being found for a given chrome content. Also, it is frequently found that the shrinkage temperature of a finished leather is much lower than that of the corresponding leather in the blue (5,6). These observations suggest that neutralizing, dyeing, fatliquoring, and drying influence the shrinkage temperature.

In order to gain further information on some of these points the relationship between chrome content and shrinkage temperature has been investigated further. In addition to its stability to hot water, the resistance of chrome leather to the detanning action of lactates present in perspiration is important, and this also has been examined. It seemed possible that the two might be related in that multipoint-fixed chrome should be the most effective in increasing hydrothermal stability and also the least readily extracted by organic acids.

EXPERIMENTAL

Raw material.—Commercial degreased pickled hair sheepskins were used for all experiments. They were depickled, acetone-dehydrated, and cut into strips 1.0 x 5 cm., all with their long axis perpendicular to the backbone.

Method of tanning.—The pieces of pelt were wet back, pickled, chrome-tanned and neutralized in stoppered bottles. All tannages were with a 33% basic chromium sulfate liquor, basified with sodium bicarbonate.

Experiments I and II.—Samples (15 g. each) of acetone-dehydrated pelt were shaken in two changes of 400 ml. 3% sodium sulfate solution, and the pH was adjusted to 3.0 with sulfuric acid. The samples were drained, and each was tanned in 400 ml. 33% basic chromium sulfate liquor with the addition of 3.5% $^{w}/_{v}$ sodium sulfate. In Experiment I the chrome content of the liquors varied from 0.004% to 1% Cr_2O_3, or the equivalent of approximately 0.1–26 g. Cr_2O_3 per 100 g. acetone-dehydrated pelt. The bottles were shaken intermittently on a rotary shaker for 48 hours, and the liquors were then slowly basified for 48 hours more to a final pH of 3.6±0.1. The samples were then rinsed in tap water and acetone-dehydrated. In Experiment II the concentration of chrome was varied between 0.01% and 2% on the liquor or about 0.25% to 50% Cr_2O_3 on dry pelt. The bottles were shaken intermittently for 24 hours, and the liquors were basified during a further period of 72 hours to final pH values of 3.7, 4.0, or 4.5. The samples were neutralized in four changes of tap water and acetone-dehydrated.

Experiment III.—Four samples (50 g. each) of acetone-dehydrated pelt were shaken in 500 ml. 3% sodium sulfate solution for 30 minutes. The solution was then changed, and the pH was adjusted to 3.0 by the addition of sulfuric acid over a further period of 4 hours. The samples were tanned as before in 500 ml. chrome liquor containing 0.3, 0.6, 1.2, or 2.4% Cr_2O_3, i.e., 3, 6, 12, and 24% Cr_2O_3 on dry pelt weight. After 6 hours of shaking they were left to stand overnight and then were slowly basified to pH 4 ± 0.05 over a period of 2 days.

The samples were washed in three 500-ml. lots of tap water, and then each was divided into three portions and neutralized as follows:

A. None
B. Shaken for 30 min. in 0.5% $NaHCO_3$ on tanned weight in 200 ml. water, followed by three changes of tap water
C. The same as B, but using 1.5% $NaHCO_3$ on tanned weight

Each of these was again subdivided and treated as below:

1. Kept wet
2. Sealed in polythene bags and placed in an incubator at 40° for 7 days
3. Dried at 20°C.
4. Dried at 40°C.
5. Dried at 60°C.
6. Dried at 80°C.
7. Dried at 20° and heated to 100°C. for 4 hours

Examination of samples.

Chrome.—Chrome was determined by the perchloric acid oxidation method (7), and results were expressed on the moisture-free weight obtained by heating for 16 hours at 105°C.

Shrinkage temperature.—The samples (5 cm. x 1 cm.) were wet back in water under reduced pressure, and the determinations were made in 75% $^{v}/_{v}$ glycerol/water mixtures. A counterweight of 10 g. was used, and the rate of heating was 1° to 2° a minute. Determinations were made in duplicate or triplicate. At temperatures above about 116°C. the water tends to boil from the glycerol. Tests, however, show that reduction in water content down to 15% (B.P. of mixture = 127°C.) has no effect on the value. Values over 130°C. are open to some doubt, as the rate of heating became very slow and the amount of shrinkage very small.

Extraction with sodium lactate.—Samples (1g. each) were extracted with 25 ml. 5% sodium lactate solution containing 5% sodium chloride for 10 days at 20°C. (Experiment II) or for five days at 50°C. (Experiment III). The samples were washed with 5 × 50 ml. water over a period of two hours and air-dried. One strip was taken for shrinkage temperature, and those remaining were dried at 105°C. for 16 hours, weighed, and used for chrome determination. Each extraction was carried out in duplicate.

RELATIONSHIP BETWEEN CHROME CONTENT AND SHRINKAGE

Two experiments were carried out in which acetone-dehydrated cape sheepskin was tanned to series of chrome contents in basic chromium sulfate liquors (for details of tannage, see "Method of tanning" above).

In both experiments the shrinkage temperature increased with the chrome content, and there was a linear relationship between shrinkage temperature and the logarithm of the chrome content, similar to that obtained by Bowes *et al.* (1). (See Fig. 1.) There were, however, slight differences in the slopes of the three lines. There were only slight variations in the tanning procedures in the two present experiments, and the only apparent reason for the reduced shrinkage temperature in relation to chrome content in the second experiment is the slower addition of bicarbonate and the more thorough neutralization of the samples.

On extraction of the leather samples from Experiment II with sodium lactate solutions a linear relationship was again found, but in this case it was displaced to lower values of shrinkage temperature (Fig. 1). This displacement is presumably due to the fact that some of the chrome is complexed with lactate and hence not able to exert its full tanning action.

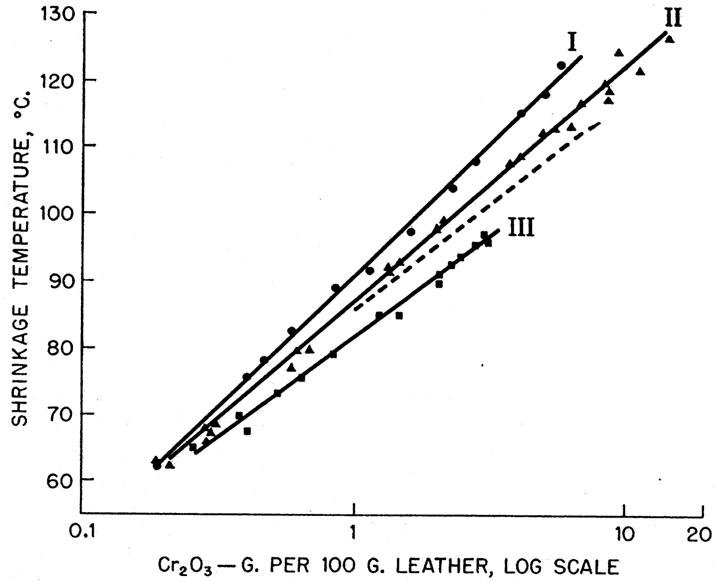

FIGURE 1.—Relationship between chrome content and shrinkage temperature.

● ——— ● Experiment I
▲ ——— ▲ Experiment II
■ ——— ■ Chrome leathers from Experiment II after extraction with sodium lactate solutions
– – – – – Taken from Bowes *et al.* (1)

Introduction of additional carboxyl groups into the collagen by treatment with formaldehyde and glycine (8) led to increased fixation of chrome and to an increase in shrinkage temperature in relation to chrome content of about 10°C. (In Fig. 2 compare curves *A* and *A′*).

$$\underset{\text{protein amide}}{\vdash CO\cdot NH_2} + HCHO + \underset{\text{glycine}}{NH_2\cdot CH_2\cdot COOH} \longrightarrow \vdash CO\cdot NH\cdot CH_2\cdot NH\cdot CH_2\cdot COOH$$

$$\underset{\text{protein guanidyl}}{\vdash NH\cdot C{\scriptstyle\begin{matrix}\diagup\!\!\diagup NH \\ \diagdown NH_2\end{matrix}}} + HCHO + \underset{\text{glycine}}{NH_2\cdot CH_2\cdot COOH} \longrightarrow \vdash NH\cdot C{\scriptstyle\begin{matrix}\diagup\!\!\diagup NH \\ \diagdown NH\cdot CH_2\cdot NH\cdot CH_2\cdot COOH\end{matrix}}$$

Similar increases were also observed in another experiment over a more limited range of chrome contents (5). (In Fig. 2, curves *B* and *B′*). These were finished leathers, and this probably accounts for their low shrinkage temperature in relation to chrome content (see p. 97) compared with that of the crust leathers examined. The introduction of new carboxyl groups into the collagen will increase the possibilities of two of these groups being suitably placed for coordination with the same chrome complex, thus forming a cross link. The increase in shrinkage temperature which results, therefore, indicates the probable importance of such cross links in determining hydrothermal stability. On the other hand, increase in pH during tannage, which also increases the number of groups available for fixation, appears to have no influence on the relationship between chrome and shrinkage temperature. It may be that only a limited number of the carboxyl groups originally present in the collagen are suitably placed for cross-linking.

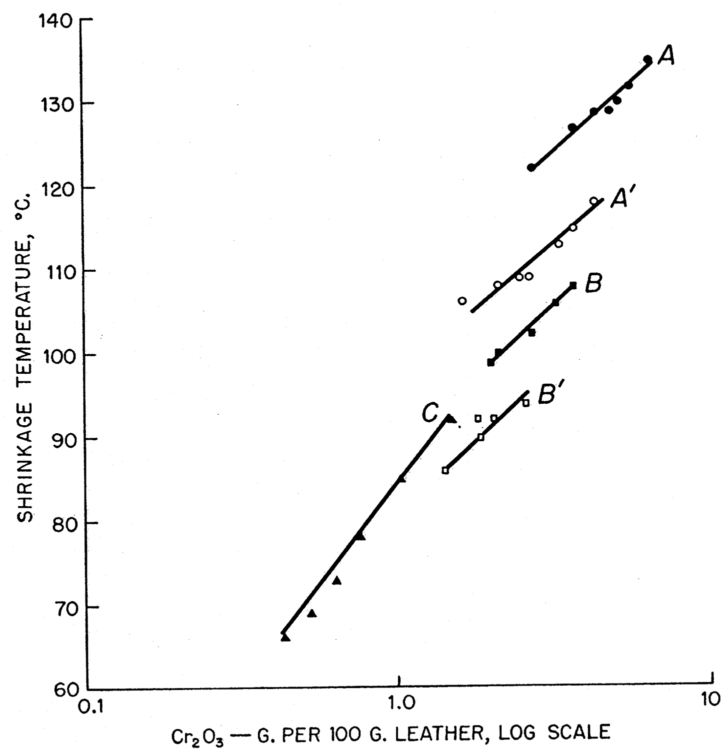

FIGURE 2.—Some factors affecting the relationship between chrome content and shrinkage temperature.

A	Pretanned with formaldehyde plus glycine—crust leather
A′	Corresponding control
B	Pretanned with formaldehyde plus glycine-dyed and finished leather
B′	Corresponding control
C	Chrome content and shrinkage temperature during successive extractions with 2% sodium lactate solutions

Earlier experiments (9) on the extraction of chrome leather with sodium lactate solutions suggest that all the chrome fixed contributes equally to hydrothermal stability, the shrinkage temperature decreasing regularly with chrome content, and it would seem that unipointly fixed chrome also plays some part (see also Fig. 2, curve *C*).

THE EFFECT OF NEUTRALIZING AND DRYING ON THE HYDROTHERMAL STABILITY AND RESISTANCE TO DETANNING BY SODIUM LACTATE

The results presented in the first section suggest that the shrinkage temperature obtained with a given chrome content may be influenced by the method of neutralizing, and other work has indicated that the method of drying may be a factor (6). It has also been observed that moist storage at 40°C. causes a slight increase in shrinkage temperature and a marked reduction in the amount of chrome which is extracted from the leather by organic acids, this effect being quite appreciable after only a few weeks (10). Samples of pelt were, therefore, tanned to various chrome contents, then either rinsed in tap water or neutralized with 0.5% or 1.5% sodium bicarbonate, and finally treated in various ways as indicated in Table I. (Experiment III—see p. 98 for details of tannage.)

The chrome contents and shrinkage temperature of the leather samples are recorded in Table I. Neutralizing slightly increased the chrome content,

TABLE I

EFFECT OF NEUTRALIZING AND DRYING ON SHRINKAGE TEMPERATURE

Tannage		Chrome Content*, % Cr_2O_3	Shrinkage Temperature, °C.						
			Wet	Dried at 20°	Dried at 40°	Dried at 60°	Dried at 80°	Dried at 20°; Heated to 100° for 4 hr.	Incubated at 40°; Dried at 20°
I	A	9.63	132	130	130	130	122	119	131
	B	9.72	130	130	132	128	120	114	130
	C	9.71	134	128	130	126	118	110	131
II	A	7.49	121	125	123	121	119	106	124
	B	7.67	124	124	121	120	117	104	124
	C	8.04	123	123	118	118	114	104	122
III	A	4.85	117	118	117	117	111	105	118
	B	5.09	118	118	117	117	110	105	117
	C	5.30	118	117	116	114	107	106	117
IV	A	2.83	110	110	110	108	104	100	112
	B	3.14	111	109	111	109	103	101	111
	C	3.16	110	106	106	105	101	101	106

*Expressed on moisture-free weight
A—rinsed in tap water
B—neutralized with 0.5% $NaHCO_3$
C— " " 1.5% $NaHCO_3$

presumably by precipitating a basic salt which was not removed in subsequent washing. This increase in chrome content was not accompanied by any rise in shrinkage temperature, however. The effect of neutralizing on the chrome–shrinkage temperature relationship is illustrated in Fig. 3 for

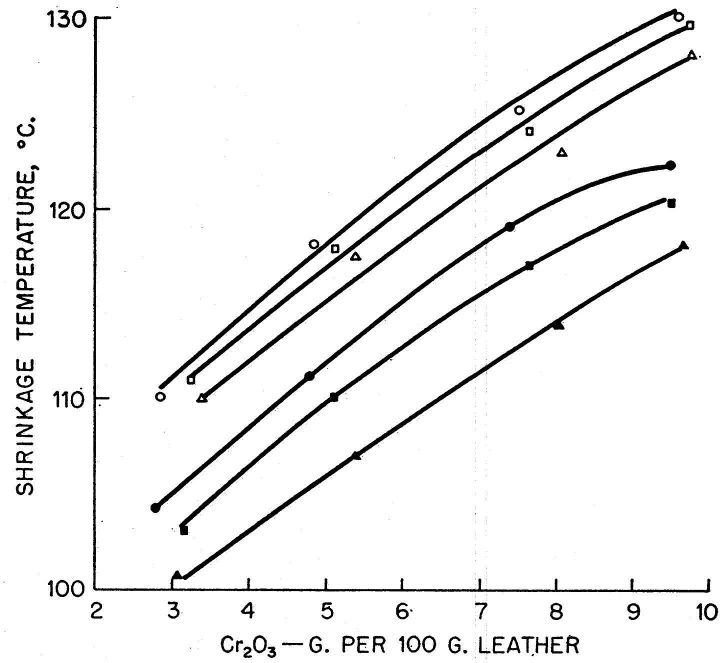

FIGURE 3.—The effect of neutralizing and drying on the relationship between chrome content and shrinkage temperature.

○ ———— ○ not neutralized
□ ———— □ neutralized with 0.5% $NaHCO_3$
△ ———— △ neutralized with 1.5% $NaHCO_3$

Open symbols dried at 20°C.
Closed symbols dried at 80°C.

the leathers dried at 20°C. and 80°C. Drying at 20°C. or 40°C., or incubating at 40°C. for 7 days, had no effect on the shrinkage temperature; drying at 60°C. caused a slight decrease of 1° to 5°, while drying at 80°C. or heating to 100°C. for 4 hours caused marked decreases. These decreases were most marked with the leathers of highest chrome content and with those most thoroughly neutralized.

The wet leathers, those dried at 20°C. and 80°C. and those incubated at 40°C. for 7 days, were tested for their resistance to the detanning action of sodium lactate solutions. The results are recorded in Tables II and III.

TABLE II

PERCENT CHROME EXTRACTED AND FALL IN SHRINKAGE TEMPERATURE (ΔTs) ON TREATMENT IN SODIUM LACTATE SOLUTIONS

	Series A	Series B	Series C	Average
Immediately after tanning	81 (36°)	81 (38°)	83 (40°)	82 (38°)
Dried at 20°	78 (35°)	81 (35°)	80 (37°)	80 (36°)
Dried at 80°	76 (23°)	73 (25°)	76 (26°)	75 (25°)
Incubated at 40°	74 (32°)	72 (30°)	61 (29°)	69 (30°)
Averages	77 (32°)	76 (32°)	75 (33°)	76 (32°)

TABLE III

CHROME CONTENTS AND SHRINKAGE TEMPERATURES AFTER EXTRACTION WITH LACTATE

	Group I		Group II		Group III		Group IV	
	$\%Cr_2O_3$	Ts °C.	$\%Cr_2O_3$	Ts °C.	$\%Cr_2O_3$	Ts °C.	$\%Cr_2O_3$	Ts °C.
Initial	9.68	130	7.73	123	5.08	118	3.04	110
Leather extracted with lactate								
Before drying	1.9	93	1.5	90	0.9	80	0.5	73
Air-dried	2.3	95	1.5	87	1.0	82	0.5	73
Dried at 80°	2.7	95	2.1	91	1.5	84	0.5	75
Incubated at 40°	3.0	101	2.4	96	1.7	87	1.0	77
A	2.78	101	1.99	95	1.30	86	0.95	76
B	2.82	102	2.21	96	1.56	88	0.81	77
C	3.47	99	3.17	96	2.29	86	1.28	78

The degree of neutralizing had little effect on the percentage of chrome extracted or on the fall in shrinkage temperature. The drying conditions, however, had a slight effect. The amounts of chrome extracted decreased progressively with drying at 20°C. or 80°C., or with incubating at 40°C., while the fall in shrinkage temperature decreased in the order: drying at 20°C., incubating at 40°C., drying at 80°C. Since drying at 80°C. reduced the shrinkage temperature in the first place, the final values for these leathers after extraction were not appreciably higher than those of the other leathers.

The final chrome content and shrinkage temperature of the four series of leathers after extraction are given in Table III. From this it may be seen that the highest chrome contents and shrinkage temperatures are obtained with leathers incubated at 40°C. With these leathers the degree of neutralization influences the final chrome content. A similar but less marked trend was shown by the leathers dried at 80°C. In neither case is the shrinkage temperature affected, which suggests that the higher retention of chrome is associated with the insolubility of basic chrome complexes precipitated in the leather on neutralization.

DISCUSSION

All the results reported here indicate that under any given conditions of tannage there is a close relationship between the shrinkage temperature and chrome content of a leather, regardless of the pH at which the chrome is fixed.

The increase in shrinkage temperature in relation to the chrome content which follows the introduction of carboxyl groups into the collagen indicates the probable importance of cross links in determining hydrothermal stability. Other evidence, however, suggests that unipointly fixed chrome also plays some part, possibly by decreasing accessibility of the fibers to water as suggested by Witnauer and Fee (3). It would be interesting to see how the shrinkage temperature in the absence of water varies with the conditions of tannage, since one might expect such measurements to be more closely related to the number of cross links. Of the factors so far examined, the degree of neutralizing and higher temperatures during or after drying tend to reduce the shrinkage temperature in relation to the chrome content. In view of the results obtained with the leathers extracted with sodium lactate solution, it seems reasonable to assume that the presence of organic acids during tanning will also have an effect. The decrease in shrinkage temperature on dyeing is also probably attributable to the same cause (6). The effect of neutralizing may presumably be ascribed to the precipitation of a basic chrome salt which has no tanning action. Why high temperatures of drying should reduce the shrinkage temperature is not clear, particularly as they have been shown to reduce swelling in water (11).

Increased resistance to the stripping action of sodium lactate solutions does not necessarily follow increases in shrinkage temperature, and the question of the greater stability of multipoint- as against unipoint-fixed chrome remains open.

The findings as a whole indicate the conditions of processing likely to give maximum hydrothermal stability and resistance to perspiration. For high thermal stability the tannage should be carried out under conditions facilitating the formation of cross links, e.g., maximum number and availability of carboxyl groups and minimum swelling, to reduce the distances between carboxyl groups in adjacent chains and the presence of relatively large chrome complexes capable of bridging these distances. Neutralization should be kept to a minimum, and the leather should be dried at temperatures below 60°C. Similar conditions of tanning should also give optimum resistance to perspiration, but in this case neutralization, drying at elevated temperatures, or keeping at 40°C. in the wet state for a short period may cause some improvement. It might be expected that tanning at raised temperatures would have a similar effect to incubation at 40°C.

ACKNOWLEDGMENTS

Thanks are due to Mr. P. Whitehead and Mr. J. C. Saunders for technical assistance and to the U. S. Department of Agriculture for permission to publish.

REFERENCES

1. Bowes, Davies, Pressley, and Robinson. *J. Soc. Leather Trades Chemists,* **31,** 236 (1947).
2. ———, quoted by Balfe and Humphreys, *Progress in Leather Science* 1920–45, British Leather Manufacturers' Res. Assoc., 1948, p.415.
3. Witnauer and Fee. *J. Soc. Leather Trades Chem,* **54,** 374 (1959).
4. Gustavson. *The Chemistry of the Tanning Processes,* (New York: Academic Press, 1956), p. 122.
5. Bowes. Unpublished.
6. Moss. In preparation.
7. Official Methods of Analysis, Soc. Leather Trades Chemists, 1951, p. 104.
8. Bowes. Unpublished.
9. ——— and Moss. *J. Soc. Leather Trades Chem,* **44,** 419 (1960).
10. Raistrick, A. S. *JALCA,* **56,** 616 (1961).
11. Greaves. Ph.D. thesis, Leeds University.

Received December 6, 1961.